SPECIAL ARTICLE

*The 72th CerSJ Awards for Advancements in Ceramic Science and Technology: Review***Low-temperature synthesis of boride powders by controlling microstructure in precursor using organic compounds**Masaki KAKIAGE^{1,†}¹Institute for Fiber Engineering, Shinshu University (IFES), Interdisciplinary Cluster for Cutting Edge Research (ICCER), Shinshu University, 3–15–1 Tokida, Ueda, Nagano 386–8567, Japan

The carbothermal reduction of boron oxide (B_2O_3) is an important process for the synthesis of boride powders. As a low-temperature synthesis method for boron carbide (B_4C) powder by carbothermal reduction, we focused on an approach using a condensed product prepared from boric acid (H_3BO_3) and an organic compound with a number of hydroxyl groups (a polyol) such as glycerin, mannitol, or poly(vinyl alcohol). A borate ester bond was formed by the dehydration condensation of H_3BO_3 and a polyol, leading to the homogeneous dispersion of the boron and carbon sources at the molecular level. The thermal decomposition of a condensed H_3BO_3 -polyol product in air was performed to control the amount of carbon to the stoichiometric C/B_2O_3 ratio required for carbothermal reduction. Within the thermally decomposed product consisting of B_2O_3 and carbon components (B_4C precursor), a B_2O_3 /carbon structure at the nanometer scale was formed. The improved dispersibility and homogeneity of the B_2O_3 /carbon microstructure accelerated the B_4C formation at a lower temperature. Consequently, crystalline B_4C powder with little free carbon was synthesized by heat treatment at a low temperature of 1200°C in an Ar flow. This low-temperature synthesis approach was applied to the low-temperature synthesis of other boride powders, i.e., boron nitride and calcium hexaboride powders.

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Key-words : Low-temperature synthesis, Carbothermal reduction, Precursor, Microstructure, Polyol, Boron carbide (B_4C), Boride powders

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1. Introduction

Carbothermal reduction is an important industrial process for the synthesis of non-oxide ceramic powders such as carbides, borides, and nitrides. The carbothermal reduction of boron oxide (B_2O_3) is the most common industrial manufacturing method for boron carbide (B_4C) powder.^{1)–3)} The overall reaction of carbothermal reduction is given by

This process is suitable for large-scale synthesis because the starting materials, which include boric acid (H_3BO_3) or B_2O_3 as a boron source and activated carbon or petroleum coke as a carbon source, are inexpensive and nonhazardous. However, this process is conducted at a high temperature of approximately 2000°C. The volatilization loss of boron components is significant at the high synthesis temperature. Furthermore, the obtained ingot must be crushed, refined, and granulated to produce B_4C powder suitable for practical use. B_4C exhibits extremely high

hardness, and thus a large amount of energy is required for the pulverization process. Therefore, the development of a low-temperature synthetic route has been strongly expected for avoiding the volatilization loss of boron components and reducing the manufacturing cost.

In order to reduce the synthesis temperature of B_4C powder by carbothermal reduction, the B_2O_3 and carbon components must be dispersed well to increase the contact area between the B_2O_3 and carbon components and to reduce the diffusion distance of the reacting species. Many studies reported to synthesize B_4C powder at lower temperatures by using a condensed product which employed various organic compounds as a carbon source such as glycerin,^{4),5)} citric acid,^{6)–8)} sugar,^{9),10)} phenolic resin,¹¹⁾ and poly(vinyl alcohol) (PVA),¹²⁾ and they could reduce the synthesis temperature to 1500–1600°C. However, in the case of heat treatment at lower temperatures of less than 1500°C, the product contained residual free carbon derived from the organic compound used as the raw material.

We have focused on both a molecular approach and a structural approach to further reduce the synthesis temperature of B_4C powder without residual free carbon using a condensed H_3BO_3 -polyol product.^{13)–19)} The compatibility of the composition, the dispersibility, and the homogeneity

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of the B_2O_3 and carbon components in a precursor was achieved by the combination of the bond-forming reaction between H_3BO_3 and a polyol and a thermal decomposition process in air (molecular approach). Furthermore, a finely and homogeneously arranged B_2O_3 /carbon structure in the precursor led to a larger interface between the B_2O_3 and carbon components, enabling synthesis of B_4C powder at a low temperature of $1200^\circ C$ (structural approach).

2. Molecular approach: formation of B–O–C bond and compositional control by thermal decomposition in air

Carbothermal reduction using a condensed product as a precursor that consists of H_3BO_3 and an organic compound with a number of hydroxyl (–OH) groups (a polyol) is attractive as a low-temperature synthetic method for B_4C . A condensed H_3BO_3 –polyol product forms a borate ester (B–O–C) bond by a dehydration condensation reaction between H_3BO_3 and the polyol [Fig. 1(a)].²⁰ The formation of this bond leads to the homogeneous dispersion of the boron source and carbon source at the molecular level, and thus the synthesis temperature is reduced owing to the increased surface-active area between the B_2O_3 and carbon components with superior reactivity. We used glycerin ($C_3H_8O_3$),^{14,19} mannitol ($C_6H_{14}O_6$),¹⁶ or PVA^{13,15,18} as a polyol that has a strong complexation ability and can easily form a B–O–C bond with H_3BO_3 .^{5,20,21} Expected molecular structures of a condensed H_3BO_3 –glycerin product,⁵ a condensed H_3BO_3 –mannitol product,²⁰ and a condensed H_3BO_3 –PVA product are shown in Fig. 1. However, the obtained product contained a large amount of residual carbon derived from the polyol, which is a common disadvantage of B_4C synthesis using an organic compound, since a condensed product has excessively large carbon component compared with that required for carbothermal reduction. In previous research,^{8,10} an excessive amount of H_3BO_3 was used as a raw material to prevent the formation of residual free carbon in the product. However, the homogeneity was low for the condensed product prepared

with excess H_3BO_3 , which contained an isolated H_3BO_3 component without a B–O–C bond.¹⁶ Therefore, the simultaneous pursuit of dispersibility and compositional control of a condensed product contains a major contradiction.

In an attempt to resolve the above contradiction, we performed the thermal decomposition in air before the carbothermal reduction of a condensed H_3BO_3 –polyol product prepared at the stoichiometric ratio for the dehydration condensation to control the amount of carbon to the stoichiometric C/ B_2O_3 ratio required for the carbothermal reduction given by Eq. (1) (C/ B_2O_3 = 3.5). The thermal decomposition in air eliminates the excess carbon component while maintaining the dispersibility. **Figure 2** shows X-ray diffraction (XRD) patterns of the products obtained by heat treatment at $1250^\circ C$ for 5 h in an Ar flow of thermally decomposed products (precursor powders) prepared from the condensed H_3BO_3 –mannitol product by thermal decomposition at (a) 300 – $500^\circ C$ for 2 h and (b) $400^\circ C$ for 1–4 h in air.¹⁶ The XRD patterns changed systematically with the thermal decomposition temperature [Fig. 2(a)] and holding time [Fig. 2(b)]. A peak attributed to amorphous carbon was observed at lower thermal decomposition temperatures or for shorter holding times, indicating that the precursor had excess carbon, and peaks attributed to B_2O_3 were observed at higher thermal decomposition temperatures or for longer holding times, indicating that the precursor had excess B_2O_3 . Note that the structural homogeneity of the condensed H_3BO_3 –mannitol product dominated the B_4C formation behavior at a low synthesis temperature (see Figs. 11 and 12 in Ref. 16). The formation of B_4C was induced simultaneously within a short time throughout the entire homogeneous precursor (the thermally decomposed product prepared from the condensed product with the stoichiometric ratio for the dehydration condensation) even at a low synthesis temperature. In contrast, widely spaced B_2O_3 and carbon components, which have less reactivity, existed in the heterogeneous precursor (the condensed product prepared with excess H_3BO_3 , which contained an isolated H_3BO_3 component without a B–O–C bond). The heterogeneity of the synthesis reaction, which reflects the structural heterogeneity, resulted in a time lag in the complete formation of B_4C , particularly at a low synthesis temperature.¹⁶ Consequently, the low-temperature synthesis of crystalline B_4C powder with little free carbon was achieved by carbothermal reduction using a condensed H_3BO_3 –polyol product with a highly and homogeneously dispersed structure and a suitable C/ B_2O_3 composition. The C/ B_2O_3 composition of the precursor can be controlled by varying the thermal decomposition conditions in air.

3. Structural approach: morphological control of B_2O_3 /carbon microstructure in precursor

The formation reaction of B_4C from a condensed H_3BO_3 –polyol product is carbothermal reduction, i.e., the reaction of B_2O_3 and carbon [Eq. (1)]. Hence, we propose an approach to developing lower-temperature synthesis routes by clarifying in detail the relation between the

Fig. 1. (a) Schematic interpretation of dehydration condensation reaction between H_3BO_3 and polyol and molecular structures of (b) condensed H_3BO_3 –glycerin product, (c) condensed H_3BO_3 –mannitol product, and (d) condensed H_3BO_3 –PVA product.

Fig. 2. XRD patterns of products obtained by heat treatment at 1250°C for 5 h in an Ar flow of precursor powders prepared from condensed H_3BO_3 -mannitol product by thermal decomposition at (a) 300–500°C for 2 h and (b) 400°C for 1–4 h in air.¹⁶⁾

precursor structure (B_2O_3 /carbon structure) and the formation of B_4C .

A thermally decomposed product consisting of B_2O_3 and carbon components (B_4C precursor) was prepared from a condensed H_3BO_3 -polyol product by thermal decomposition in air. Within the obtained precursor prepared from the condensed H_3BO_3 -polyol product under suitable conditions, a three-dimensional networked carbon structure with a homogeneous B_2O_3 /carbon arrangement at the nanometer scale was spontaneously formed. **Figure 3** shows scanning electron microscope (SEM) images of the precursors prepared from (a, b) the condensed H_3BO_3 -glycerin product¹⁴⁾ and (c, d) the condensed H_3BO_3 -PVA product.¹⁵⁾ The B_2O_3 component can be removed by washing the precursor powder in hot water, thus leaving the carbon component, as shown in Figs. 3(b) and 3(d). A characteristic carbon network structure with nano-order spacing can be recognized for both precursors. A three-dimensional bicontinuous structure composed of B_2O_3 and carbon components was formed for the condensed H_3BO_3 -glycerin product [Fig. 3(b)]. On the other hand, nanosize B_2O_3 particles were dispersed in a carbon matrix for the condensed H_3BO_3 -PVA product [Fig. 3(d)]. The B_2O_3 /carbon microstructure is beneficial for the low-temperature carbothermal reduction of B_2O_3 , coupled with the dispersibility of the boron and carbon sources. The formation of a homogeneously arranged B_2O_3 /carbon structure at the nanometer scale contributes to its markedly increased contact area without the powder compaction of the raw materials. Furthermore, the networked carbon structure prevents the aggregation of molten B_2O_3 liquid (melting point: 450°C) during the heat treatment, leading to an enlarged surface-active area and the efficient removal of

Fig. 3. SEM images of precursors prepared from (a, b) condensed H_3BO_3 -glycerin product¹⁴⁾ and (c, d) condensed H_3BO_3 -PVA product¹⁵⁾ (a, c) before and (b, d) after removal of B_2O_3 by washing in hot water.

the byproduct CO gas. Therefore, the synthesis temperature is expected to be lowered by improving the dispersion state of the B_2O_3 and carbon components owing to the increased surface-active area between the B_2O_3 and carbon components, resulting in higher reactivity.

The precursor prepared from the condensed H_3BO_3 -glycerin product formed a characteristic three-dimensional bicontinuous structure composed of B_2O_3 and carbon

Fig. 4. SEM images of precursors prepared from condensed H_3BO_3 -glycerin product (a) without and (b) with TA added after removal of B_2O_3 by washing in hot water.¹⁹⁾

components [Fig. 3(b)]. Glycerin is an organic solvent of low molecular weight; thus, homogeneous blending can be easily achieved with an organic compound. Therefore, we attempted to further develop the precursor structure by the multicomponent blending of organic compounds to obtain a precursor with a more homogeneously and finely dispersed B_2O_3 /carbon structure derived from the condensed H_3BO_3 -glycerin product.¹⁹⁾ Tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, TA) was adopted as the organic compound added to the condensed H_3BO_3 -glycerin product because of its two hydroxyl and two carboxyl groups, low molecular weight, and solubility in glycerin. **Figure 4** shows SEM images of the precursors prepared from the condensed H_3BO_3 -glycerin product (a) without and (b) with TA added after the removal of B_2O_3 by washing in hot water.¹⁹⁾ The precursor prepared from the condensed H_3BO_3 -glycerin product with TA added [Fig. 4(b)] had a more homogeneously and finely dispersed bicontinuous B_2O_3 /carbon structure. This is because the hydroxyl groups enabled the chemical structure of the complex condensed product to be continuously formed, and the carboxyl groups separated the H_3BO_3 parts. **Figure 5** shows XRD patterns of the products obtained by heat treatment of these precursor powders at 1250°C for 3 h in an Ar flow.¹⁹⁾ The complete formation of crystalline B_4C powder was achieved at 1250°C within a shorter heat treatment time for the precursor with a fine dispersion state [Fig. 4(b)] because the diffusion of reacting species became easier with increasing contact area of the B_2O_3 and carbon components.

The morphology of the precursor obtained by the thermal decomposition of the condensed H_3BO_3 -PVA product in air consisted of B_2O_3 particles dispersed in a carbon matrix [Fig. 3(d)], which is similar to the sea-island structure of a polymer alloy. It is known that the phase-separated morphology of a polymer alloy is related to the volume fraction of each component. Furthermore, the number of hydroxyl groups, which react with H_3BO_3 , increases with increasing PVA content, increasing the dispersion of H_3BO_3 . Thus, we considered the effect of the PVA content of the condensed H_3BO_3 -PVA product on the microstructure in the precursor and the formation of B_4C at a low synthesis temperature.¹⁸⁾ **Figure 6** shows SEM images of the precursors prepared from the condensed

Fig. 5. XRD patterns of products obtained by heat treatment at 1250°C for 3 h in an Ar flow of precursor powders prepared from condensed H_3BO_3 -glycerin product (a) without and (b) with TA added (corresponding to Fig. 4).¹⁹⁾

Fig. 6. SEM images of precursors prepared from condensed H_3BO_3 -PVA product with (a) lower and (b) higher PVA contents after removal of B_2O_3 by washing in hot water.¹⁸⁾

H_3BO_3 -PVA product with (a) lower and (b) higher PVA contents after the removal of B_2O_3 by washing in hot water.¹⁸⁾ The dispersibility of B_2O_3 particles in the carbon matrix markedly improved with increasing PVA content of the condensed product. H_3BO_3 molecules were more finely dispersed in the network of the condensed product with increasing PVA content. Consequently, the aggregation of B_2O_3 was suppressed and a precursor having a finely and homogeneously dispersed structure was fabricated. **Figure 7** shows XRD patterns of the products obtained by heat treatment of these precursor powders at 1200°C for 5 h in an Ar flow.¹⁸⁾ Crystalline B_4C powder with little free carbon was synthesized at 1200°C for 5 h from the precursor with a more finely and homogeneously dispersed structure [Fig. 6(b)], which is the lowest temperature reported for the synthesis of B_4C powder by carbothermal reduction. These results demonstrate that the synthesis temperature and holding time can be reduced by using a precursor with a finely and homogeneously dispersed B_2O_3 /carbon structure because the diffusion of the reacting species became easier with increasing contact

area of the B_2O_3 and carbon components and decreasing diffusion distance of the reacting species.

Figure 8 shows SEM images and particle size distributions of the products obtained by heat treatment at 1250°C for 5 h in an Ar flow from (a, b) the condensed H_3BO_3 -mannitol product,¹⁶⁾ (c, d) the condensed H_3BO_3 -glycerin product,¹⁹⁾ and (e, f) the condensed H_3BO_3 -PVA prod-

Fig. 7. XRD patterns of products obtained by heat treatment at 1200°C for 5 h in an Ar flow of precursor powders prepared from condensed H_3BO_3 -PVA product with (a) lower and (b) higher PVA contents (corresponding to Fig. 6).¹⁸⁾

uct.¹⁸⁾ B_4C powder was obtained without a postgrinding process in each case. Interestingly, the particle size differs according to the polyol used. Fine B_4C powder with submicrometer-size particles was obtained for the products prepared using mannitol ($D_{50} = 0.8\ \mu\text{m}$) and glycerin ($D_{50} = 0.9\ \mu\text{m}$). On the other hand, the grain growth of B_4C particles was observed for the product prepared using PVA ($D_{50} = 10.0\ \mu\text{m}$). This result implies that the structural morphology of the precursor affected the morphology of the B_4C particles.¹⁷⁾

4. Application to low-temperature synthesis of other boride powders: BN and CaB_6 powders

Boron nitride (BN) powder is obtained by the heat treatment of a compacted B_2O_3 -carbon mixture (pellet) in a N_2 flow (carbothermal nitridation),^{22)–25)} for which the overall reaction is given by

The B_2O_3 /carbon structure is beneficial for the low-temperature synthesis of BN powder by carbothermal nitridation using N_2 gas. The contact area of the B_2O_3 , carbon, and N_2 gas components is much larger than that obtained by conventional powder compaction. Furthermore, the networked carbon structure prevents the spread of molten B_2O_3 liquid. **Figure 9** shows XRD patterns of the products obtained by heat treatment of the precursor powder prepared from the condensed H_3BO_3 -PVA product and the directly mixed powder consisting of B_2O_3 and

Fig. 8. SEM images and particle size distributions of products obtained by heat treatment at 1250°C for 5 h in an Ar flow from (a, b) condensed H_3BO_3 -mannitol product,¹⁶⁾ (c, d) condensed H_3BO_3 -glycerin product,¹⁹⁾ and (e, f) condensed H_3BO_3 -PVA product.¹⁸⁾

Fig. 9. XRD patterns of products obtained by heat treatment of precursor powder and directly mixed powder at 1200°C for 10 h in a N₂ flow.²⁶⁾

activated carbon at 1200°C for 10 h in a N₂ flow.²⁶⁾ The BN formation was accelerated for the product obtained from the precursor powder, which had a finely dispersed B₂O₃/carbon structure. This demonstrates that the formation of the B₂O₃/carbon structure is effective for the low-temperature carbothermal nitridation.

Calcium hexaboride (CaB₆) powder is synthesized under vacuum at above 1400°C using calcium carbonate (CaCO₃), B₄C, and carbon powders as starting materials (B₄C method).^{27)–29)} On the other hand, the formation of CaB₆ by carbothermal reduction without the use of B₄C requires a high synthesis temperature of above 1700°C.³⁰⁾ Note that this process includes the transient formation of B₄C. Here, the formation temperature of B₄C is high (above 1500°C), suggesting that the transient formation of B₄C is the rate-determining step in this process. Thus, we propose a new low-temperature synthesis approach for CaB₆ powder without the use of B₄C as a raw material by the carbothermal reduction of a calcium oxide (CaO)–B₂O₃–C system [Eq. (3)] using the above-mentioned low-temperature synthesis method for B₄C powder.^{31),32)}

Figure 10 shows XRD patterns of the products obtained by heat treatment of a mixture of the thermally decomposed product prepared from the condensed H₃BO₃–PVA product and CaCO₃ powder and the directly mixed powder consisting of CaCO₃, B₂O₃, and activated carbon at 1400°C for 5 h in an Ar flow.³¹⁾ Peaks attributed to CaB₆ were observed only for the product obtained using the thermally decomposed product, indicating that the B₂O₃/carbon structure is essential for the formation of CaB₆ at a lower temperature. The transient formation of B₄C occurred at a low temperature of 1200°C.^{31),32)} CaB₆ was formed via the transient formation of calcium borate (Ca₃B₂O₆) and B₄C,^{31),32)} and CaB₆ powder with fine

Fig. 10. XRD patterns of products obtained by heat treatment of mixture of thermally decomposed product and CaCO₃ powder and directly mixed powder at 1400°C for 5 h in an Ar flow.³¹⁾

particles was synthesized by heat treatment at 1400°C for 3 h in an Ar flow.³²⁾ These results demonstrate that the B₂O₃/carbon structure prepared from a condensed H₃BO₃–polyol product by thermal decomposition in air is a suitable precursor for the low-temperature synthesis of boride powders by carbothermal reduction.

5. Summary

In this review, our approach to the low-temperature synthesis of boride powders, i.e., B₄C, BN, and CaB₆ powders, by controlling the B₂O₃/carbon microstructure in the precursor using a condensed H₃BO₃–polyol product was outlined. We focused on the formation of a B–O–C bond by the dehydration condensation of H₃BO₃ and a polyol and the formation of the B₂O₃/carbon structure by the thermal decomposition of a condensed product in air. The dispersion morphology of the B₂O₃/carbon structure is the main factor determining the synthetic process of B₄C powder. The improved dispersibility and homogeneity of the B₂O₃/carbon microstructure was conducive to the accelerated B₄C formation at lower temperatures, and the low-temperature synthesis of crystalline B₄C powder with little free carbon was achieved. This approach is a promising methodology for the low-temperature synthesis of boride powders by carbothermal reduction.

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